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The matrix effect upon both arc temperature and electron pressure

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In the last few years, literature allows poor information on the behaviour of different substances with different arc parameters (e.g temperature, electron pressure, degree of ionization,.....etc).
The present paper explains the relationship between matrix type together with matrix concentration and two of the parameters which are arc temperature and electron pressure. Similarly it shows the resultant effect produced upon line intensity of examples of both volatile and involatile elements.

1. INTRODUCTION

In spectrochemical analysis, a change in the composition of arc specimen, naturally alters the composition of the arc gas. Consequently the arc temperature and electron pressure vary. In fact, temperature governs excitation, ionization and dissociation of atoms and molecules. For that reason, any change of arc temperature will naturally effect the intensity of spectral lines in different amounts.

Previous publications described different methods for the determination of arc temperature*, while other publications described the relationship between line intensity and the calculated arc temperature**.

In this paper, a study is performed about the effect of change of both the matrix and its concentration upon the arc temperature and the electron pressure. The resultant impression produced on line intensity of both volatile and involatile elements is also studied. The temperature was measured using the two spectral lines method. Zinc was used as thermometric element.

It was only recently that the part played by electron density in excitation theory was recognized in spectro-chemistry. Yet still arguments about this important parameters are discussed***.

The electron pressure was measured using the intensity ratio of ion-atom line pair of magnesium, which used as manometric element. The measurement was performed in the middle portion of the arc gap.

*Ref. No. 2, 3, 11, 13, 17 & 19.
**Ref. No 4, 6, 7 & 8.
***Ref. No 6, 9, 16 & 20.

The matrices were selected to represent the most familiar base in an enormous diverse number of ore minerals. The study handled four different matrices.

1. Aluminium oxide.
2. Calcium carbonate.
3. Silicon dioxide
4. Sodium carbonate

Two groups of trace elements according to their volatility, were subjected to study.

(a) Volatiles : Arsenic (As), Copper (Cu), Lead (Pb), Gallium (Ga), and Silver (Ag).

(b) Involatiles : Cobalt (Co), Zirconium (Zr), Molybdenum (Mo), Nickel (Ni) & Ytrium (Y).

The variation in intensity of trace elements were also studied in four different dilutions of each matrix. The dilutions were performed with spec-pure graphite yielding percentage ratios 12.5, 25, 50 & 75% of each matrix.

Theory

The temperature and electron pressure were measured following Boumans formula (1966).

Experimental Arrangements

Equipment : The main apparatus used for this study were :

(a) Spectrograph : A medium quartz u.v. spectrograph (Zeiss Q24), its reciprocal dispersion at 3100Å is 13.0 Å/mm. The light from the arc is focused on the collimator of the spectrograph by means of three condensing achromatic lenses placed in front of the slit.

(b) Excitation source : An interrupted arc generator Carl Zeiss Jena ABR 3 provicing d.c. current 1-15 ampers.

(c) Photographic plate : ORWO blue extra hard emulsion plates were used. These were developed for 4 minutes at 18°C in freshly prepared ORWO 1 developer diluted 1 : 1 with distilled water using a thermostatically controlled developing machine.

Standards preparation :

Four dilutions from each matrix were prepared. Spec-pure powder graphite was used as a diluent to obtain standard with 12.5, 25, 50 & 75% of matrix. The trace elements (volatiles & involatiles) were inserted in each standard at equal amount. Hence any change in the intensity of the line of these elements will be only due to the change of matrix. Table (1) represents the trace elements and the compounds used and the percentages present in each standard.

The final preparation of standards were finished by adding graphite to each diluted matrix in the ratio (1 : 3) Gr : matrix.

Selection of spectral lines : spectral line have been selected in such a way to be free from interference (Harrison, 1933). The wavelength of these selected lines are given in table (1) also.

Excitation conditions : The following conditions were found to be the most suitable.

Excitation 220 V. d.c arc anode excitaton.

Current : 9 amperes, To prevent ejection of sample the current was started with 4A, and within 2 seconds it was increased to 9A.

Gap width : 3.0 mm.

Slit height : 1.0 mm for each step of the filter.

Slit width : 0.01 mm.

Filter : 3 step filter (100, 50 & 10 transmission)

Exposure time : 120 & 150 seconds for the volatiles and involatiles respectively.

Sample electrode : 20/4.6/3.3 mm. graphite, 5 mg. powdered graphite at that top of the crater.

Counter electrode : 20/4.6 nm. with a conical end.

Photometry : The optical density scale from 0–∞ was used.

Table 1

Group	Compound used	Percentage ratio present in each matrix	Measured wavelength	
Volatiles	As_2O_3	1.0 %	2349.84 A°	(a)
	AgCl	0.05	3280.68	(c)
	CuO	0.05	3273.96	(a)
	PbO	0.05	2833.07	(a)
	Ga_2O_3	0.05	2874.24	(a)
	ZnO	0.8	-- --	
	MgO	0.005	—	
Involatiles	Co_3O_4	0.30	3044.01	(a)
	MoO_3	1.0	2816.15	(a)
	NiO	0.3	3414.77	(b)
	ZrO_2	1.0	8571 39	(a)
	Y_2O_3	1.0	3203.00	(a)
	ZnO	0.8	——	
	MgO	0.005	——	

(a) This line was read in 100% transmission.
(b) This line was read in 50% transmission.
(c) This line was read in 10% transmission.

The emulsion calibration curve : A recent and more developed method "reduced blackening curve" (Kantor, 1965) is applied for the emulsion calibration curve. The contrast factor of the emulsion (γ) was slightly increased from lower to higher wavelength. Its value was 0.92 at lower wavelength (2800 A°) and 1.02 at higher wavelength (3400 A°). The preliminary curve and the calibration curve for one of the regions (3200–3400 A°) are shown in Fig. (1).

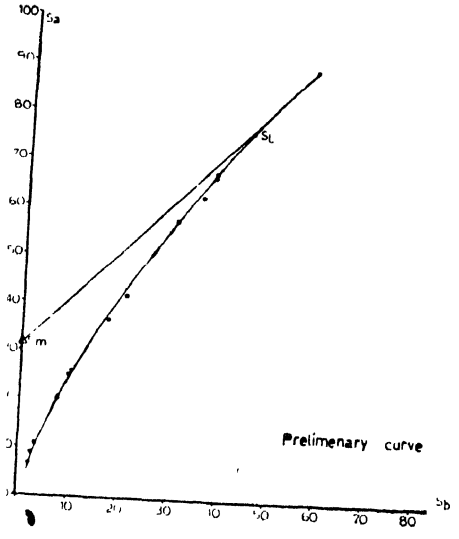


Fig. 1(a)

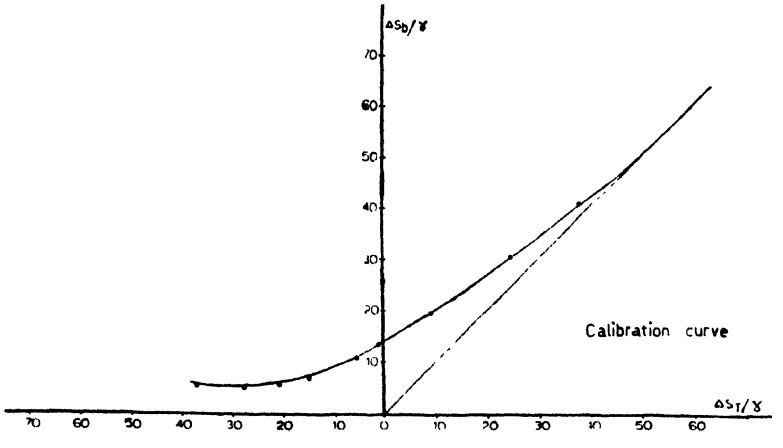


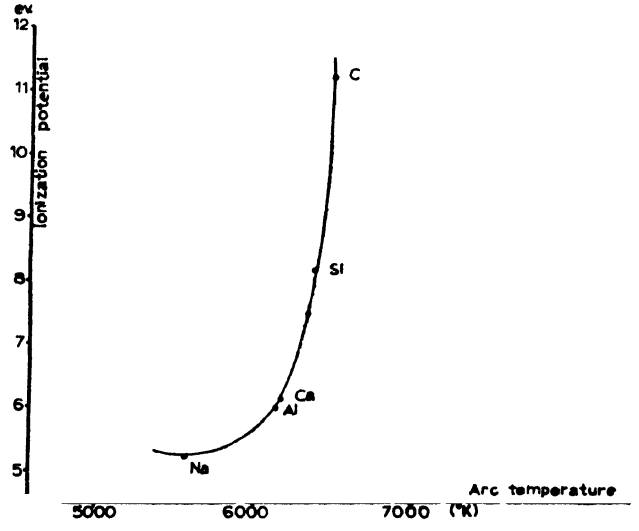
Fig. 1. The preliminary curve and the calibration curve for region 3200—3400 Å.

Background correction : Using (Kaiser, (1965) tables, correction for the background was performed on both sides of each spectral line.

Results and Discussion

(A) *Effect of change of matrix type upon arc temperature and electron pressure* :

Figure. 2 represents the relation between calculated arc temperature and the ionization potential of each matrix at 75% buffer concentration. The arc temperature increases with the ionization potential of the constituent gas of the arc column. It is obvious that maximum temperature is obtained with carbon arc which possesses the highest ionization potential The result obtained from this work agrees with that previously obtained by semenova. O.P (1946) and Addink, N.W.H. (1957). While in case of electron pressure the relation is differ. This is clear from Figure. 3. The electron pressure exhibits maximum peak with silicon dioxide and calcium carbonate matrices.



Arc temperature and ionization

Fig. 2. Relation between calculated arc temperature and the ionization potential of each matrix.

(B) *Effect of change of matrix concentration upon arc temperature and electron pressure* :

The result obtained about the temperature of the arc of various dilutions of each matrix is given in Figure. 4. It is clear that the behaviour of arc temperature differs with different matrices : from Figure. 4 both *aluminium oxide* and *calcium carbonate* show a slight increase in arc temperature with increasing the concentration of matrix.

Silicon dioxide : with the increase of silicon the concentration till 50% a fixed effect of arc temperature occured. Further addition of silicon concentration causes appreciable increase in the arc temperatures.

Sodium carbonate : It is clear that such a matrix introduces the least arc temperature. This result is in accordance with the result previously achieved by Huldt, L. (1948). The curvature of sodium carbonate matrix have concave shape. Intermediate dilutions affords relatively lower temperature.

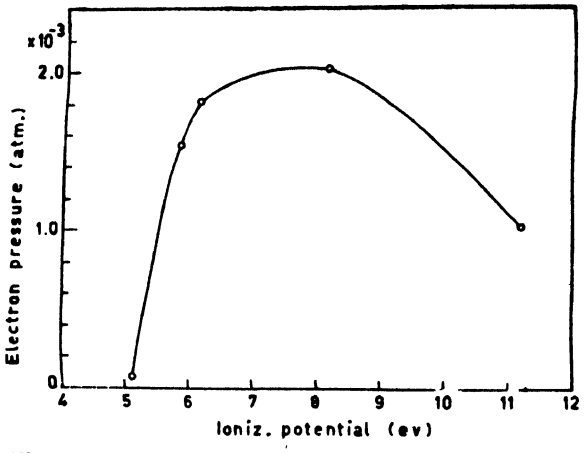


Fig. 3. Electron pressure and ionization potential of different matrices.

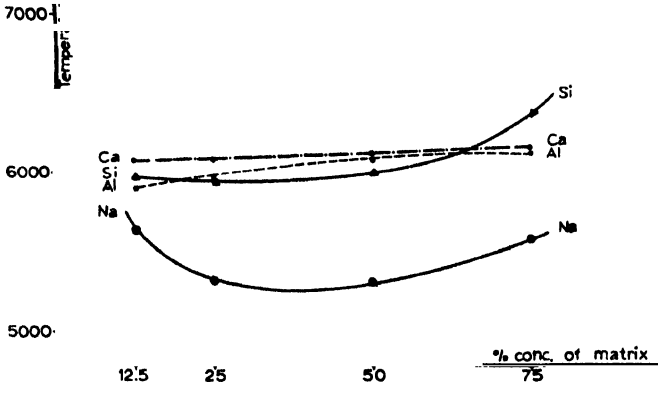


Fig. 4. Relation between various dilutions of each matrix and the arc temperature.

The behaviour of the electron pressure for the different dilutions of each matrix differs from the behaviour in case of temperature. This is shown from Figure. 5.

Aluminium oxide and silicon dioxide matrix : it is obvious that with the increase of concentration of these two matrices till 50% a nearly fixed value of electron pressure occured. Further addition of concentration causes appreciable increase in the electron pressure.

Calcium carbonate : A slight increase of the electron pressure occured with increase of calcium carbonate concentration till 50% Further addition of this matrix is accompanied by appreciable increase of the electron pressure.

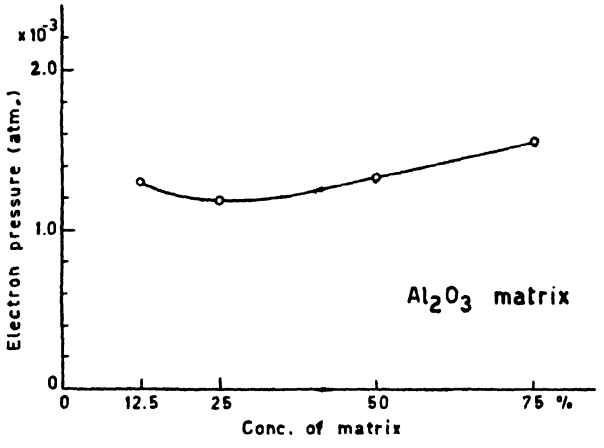


Fig. 5(a)

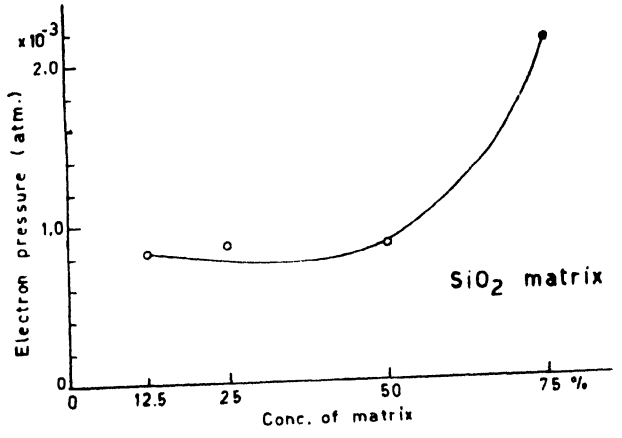


Fig. 5(b)

Sodium carbonate : sodium carbonate matrix exhibits the lowest values of electron pressure. A distinct phenomena is the constancy of the value of the electron pressure through concentration range between 25–75%.

(C) *Statistical calculation of the arc temperature and electron pressure.*

From replicate determinations, the standard deviation and relative deviation for the temperature and electron pressure of one of the matrices (at 75% $CaCO_3$) are given as an example.

Temperature = 6180°K electron pressure = 1.35×10^{-5} atm.

standard deviation $S = \pm22$°K = $\pm0.03\times10^{-5}$ atm.

relative deviation $D = \pm0.36\%$ = $\pm2\%$.

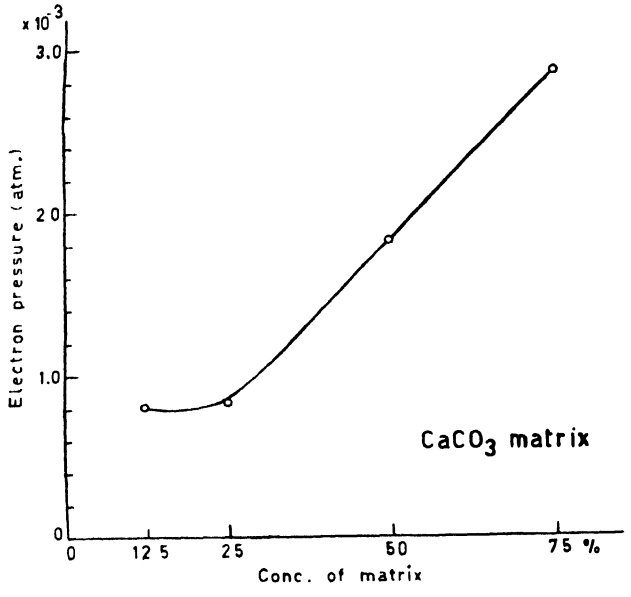


Fig. 5(c)

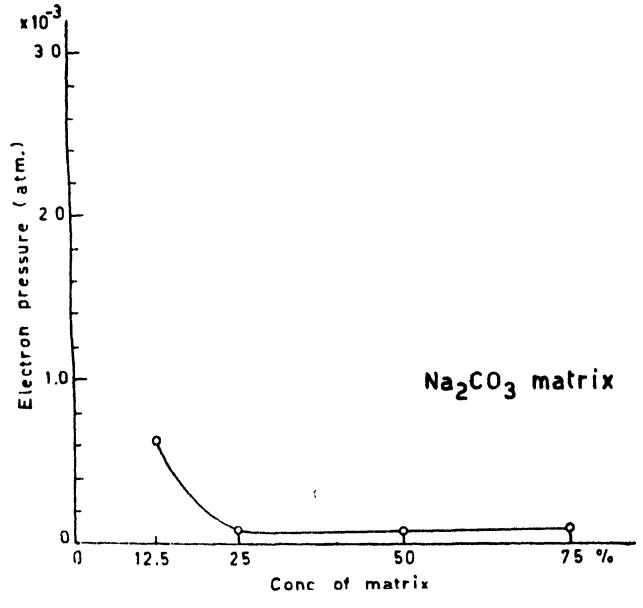


Fig. 5. Electron pressure and concentration of matrix in percent.

It is clear that the deviation is relatively small. As a result one can say that certainly the used method for temperature and electron pressure measurements is reproducible.

(D) *Effect of change of matrix electron pressure upon temperature* :

In 1965 De Galan found that under certain operating conditions, a positive correlation between the temperature and the electron pressure exists. In this work it is apparent from Figure (6) that for each matrix the electron pressure exhibits a nearly constant value for the first 150°K. Further increase of temperature is always followed by an increase in the electron pressure.

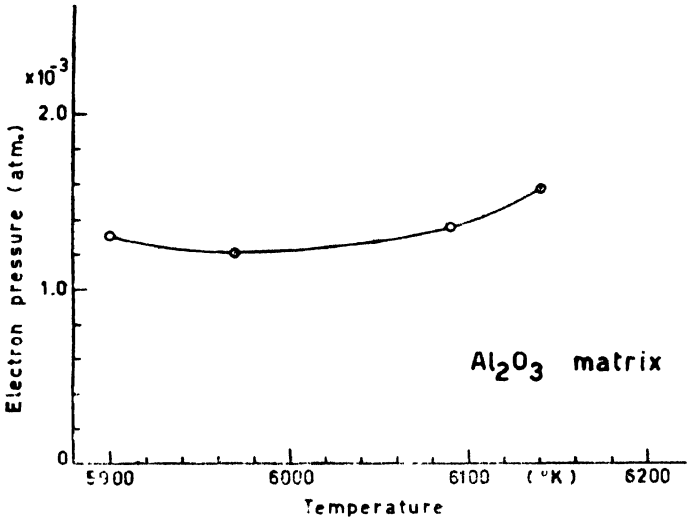


Fig. 6(a)

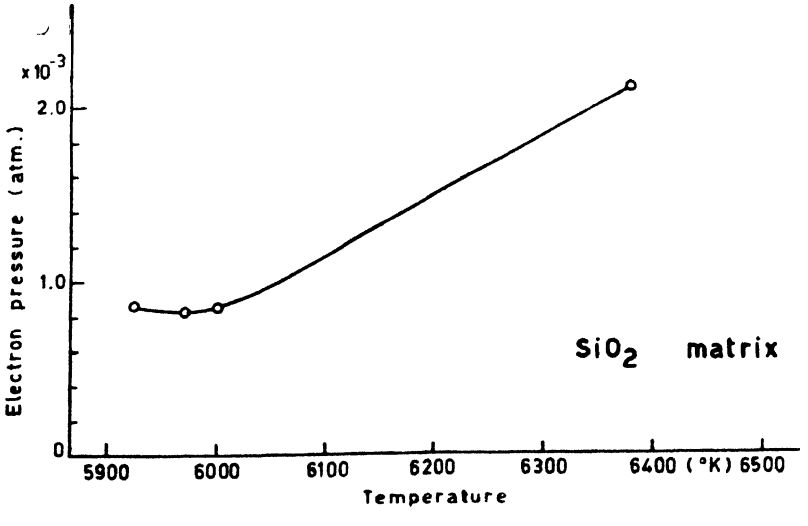


Fig. 6(b)

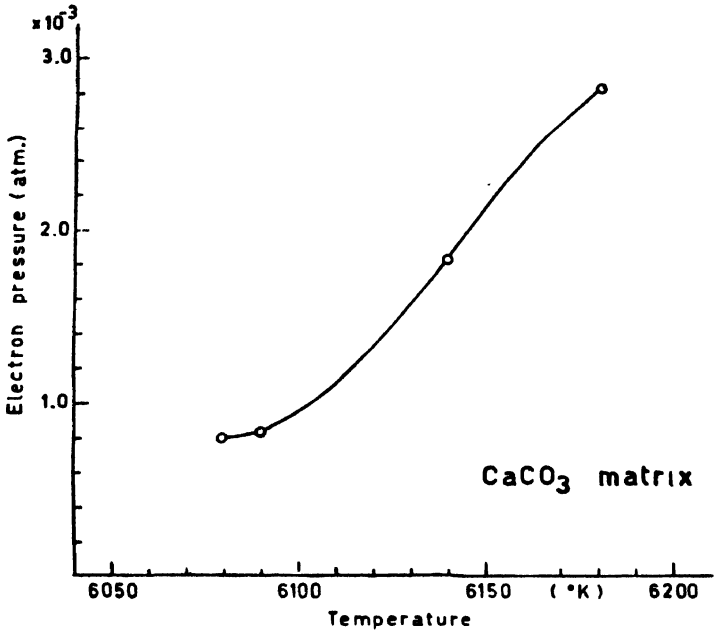


Fig. 6(c)

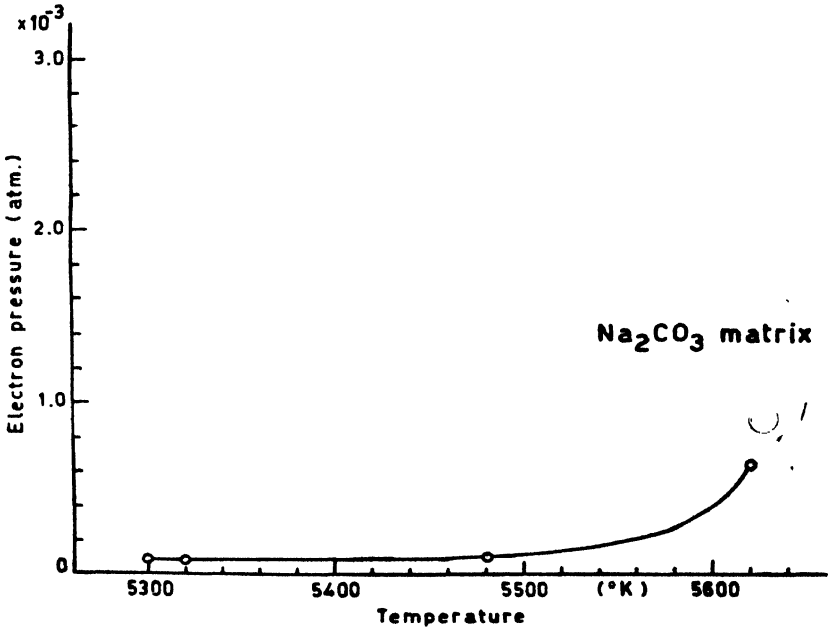


Fig. 6. Relation between matrix electron pressure and arc temperature.

(E) *Effect of change of matrix upon line intensity* :

It is clear from Figures 7 & 8 that each type of matrix yielding a certain arc temperature has a specific effect on line intensity of each element. The intensity of all elements (either volatiles or involatiles) behaves in a similar manner with the different matrices. Generally the intensity is at a maximum with aluminium oxide temperature, calcium carbonate temperature affords lower maxima. Intermediate intensity appears with silicon dioxide temperature. Minimum intensity occurs with sodium carbonate and graphite temperature.

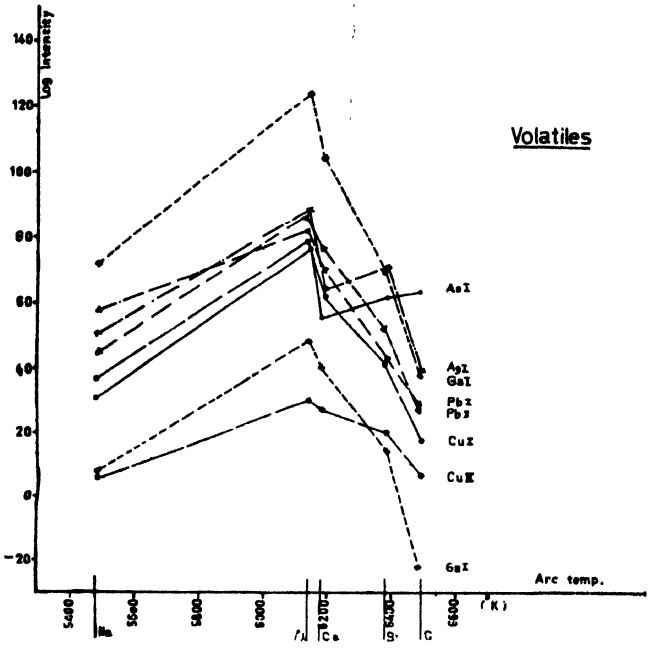


Fig. 7. Temperature of various matrices and intensity of volatile elements.

(F) *Effect of change of different dilutions of matrix and the resultant temperature and electron pressure upon line intensity* :

Results obtained from the change of line intensity with the temperature produced from different dilutions of each matrix with graphite are shown in Figures (9), (10), (11) & (12) for the volatile and involatile elements.

Aluminium oxide Figure 9. a gradual enhancement of intensity of the volatile elements occurs with the increase of arc temperature. The same behaviour realizes for the involatiles with the exception of the first observation.

Calcium carbonate Figure 10. Calcium carbonate matrix affords a reasonable temperature values within which the intensity of either volatile or involatile elements exhibits maximum intensity.

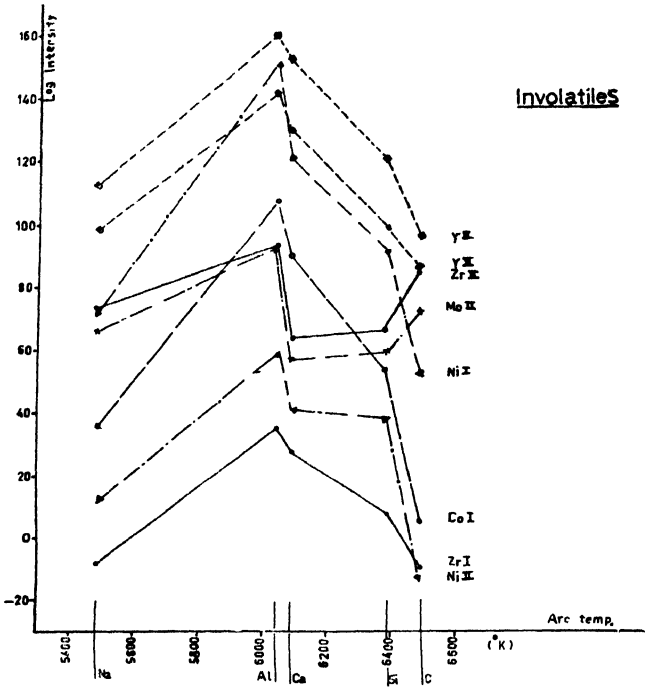


Fig. 8. Temperature of various matrices and intensity of involatile elements.

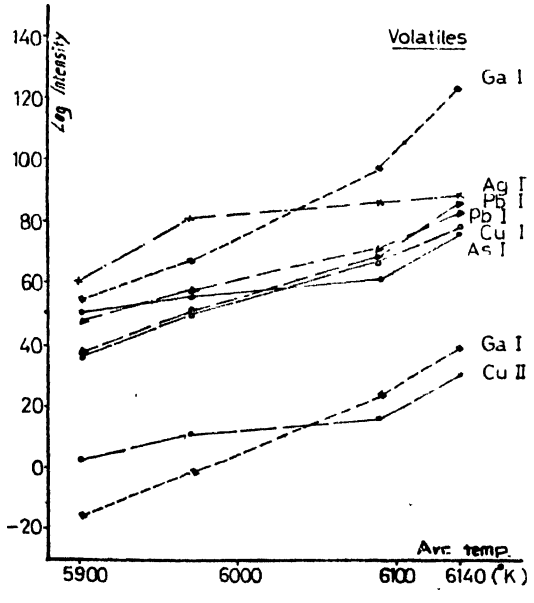


Fig. 9(a)

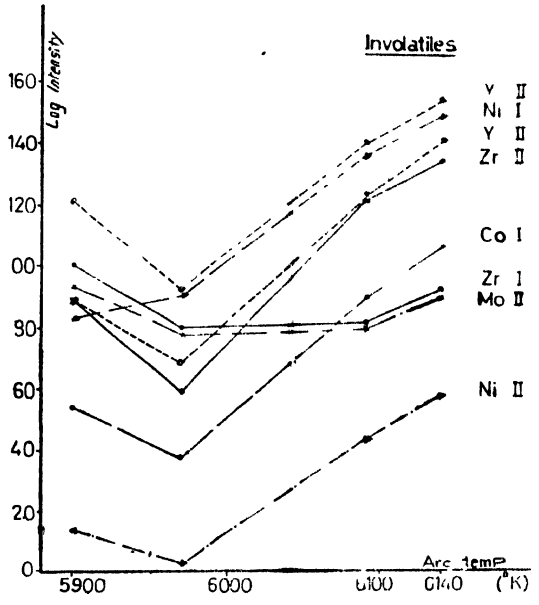


Fig. 9. Line intensity and temperature of Al_2O_3 matrix.

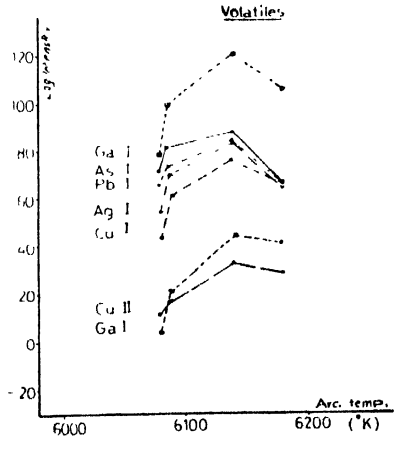


Fig. 10(a)

Silicon dioxide Figure 11 : A nearly constant intensity of either volatile or involatile elements occurs with silicon dioxide matrix for a temperature range between 5900 & 6000°K, minimum intensity appears.

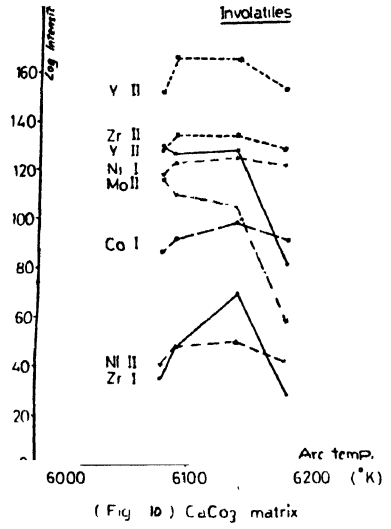


Fig. 10. Line intensity and temperature of $CaCO_3$ matrix.

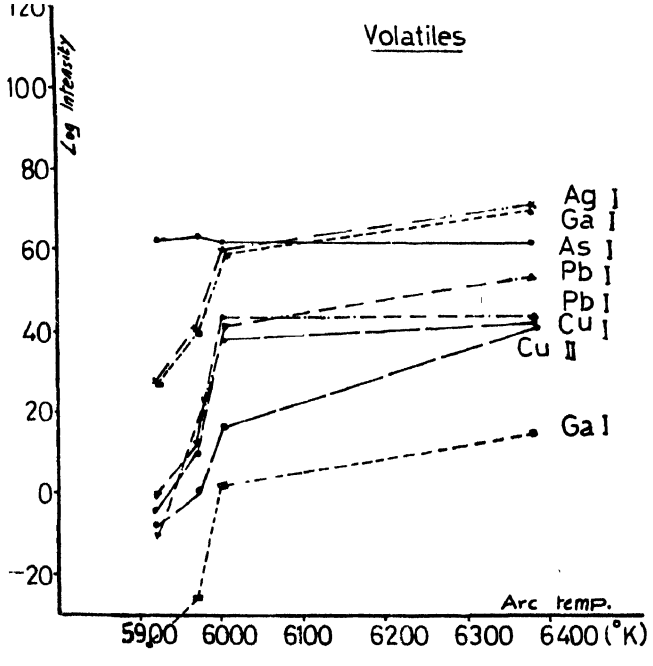


Fig. 11(a)

Sodium carbonate Figure 12 : Generally the curvature of the intensity of volatile elements shows a concave shape with minimum intensity of an intermediate value. On the contrary the curvature of involatiles shows a convex shape.

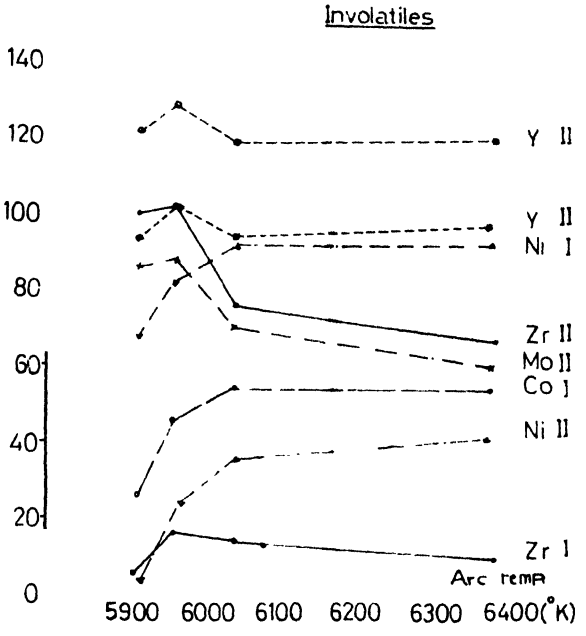


Fig. 11. Line intensity and temperature of SiO_2 matrix.

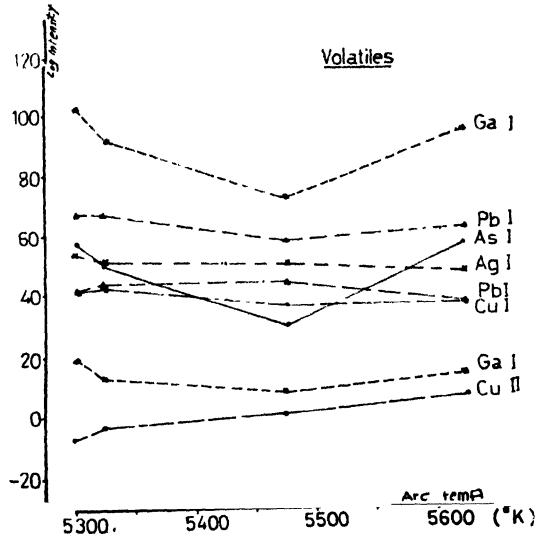


Fig. 12(a)

The behaviour of the variation of line intensity with electron pressure does not constitute a definite function relationship. This is clear from Figures 13, 14, 15 & 16. In fact this dispersion does not result from measuring errors. It should

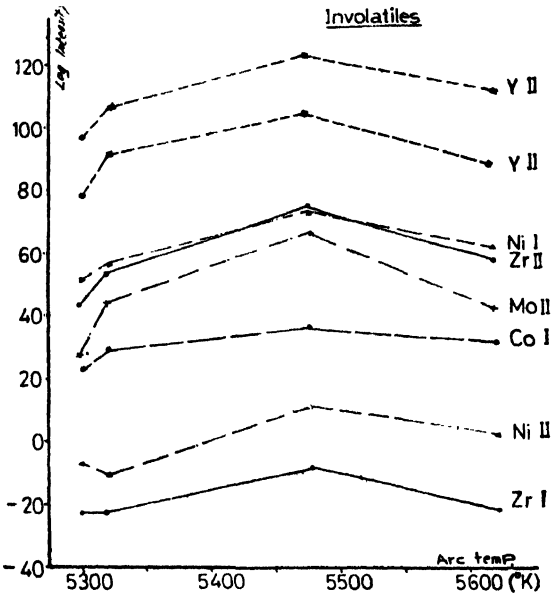


Fig. 12. Line intensity and temperature of Na_2CO_6 matrix

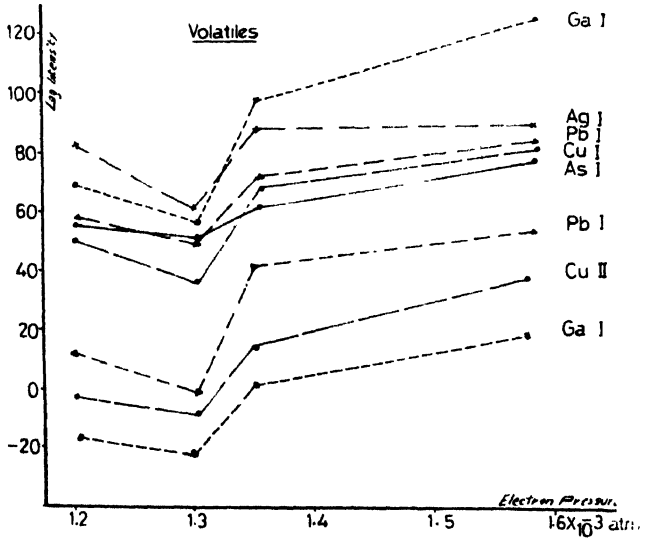


Fig. 13(a)

be considered as an essential feature. The reason could be that the difference in volatility may give rise to markedly different evaporation rates and vapour concentration.

A remarkable notice is the great variation (either increase or decrease) in intensity with the commencement value of electron pressure for each matrix. Further increase in the electron pressure causes a constant effect. Yet in the following, the effect of variation of electron pressure produced by different dilutions of each matrix upon line intensity is presented.

Aluminium oxide Figure 13 : Aluminium oxide matrix affords the least range of electron pressure. It varies between 1.17×10^{-3} (atm.). Yet this matrix provides the highest intensity for both volatile and involatile elements.

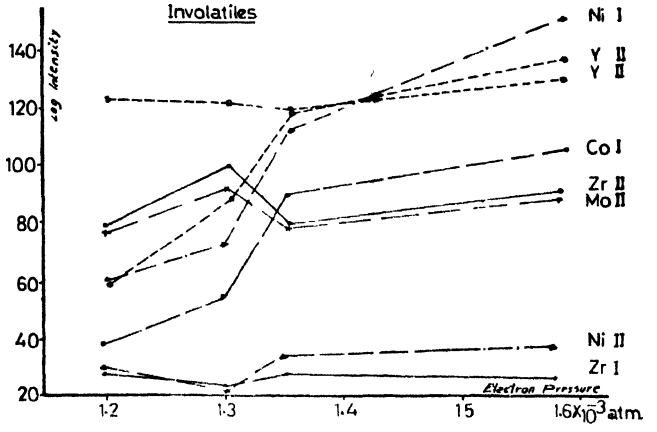


Fig. 13. Line intensity and electron pressure in case of Al_2O_3 matrix.

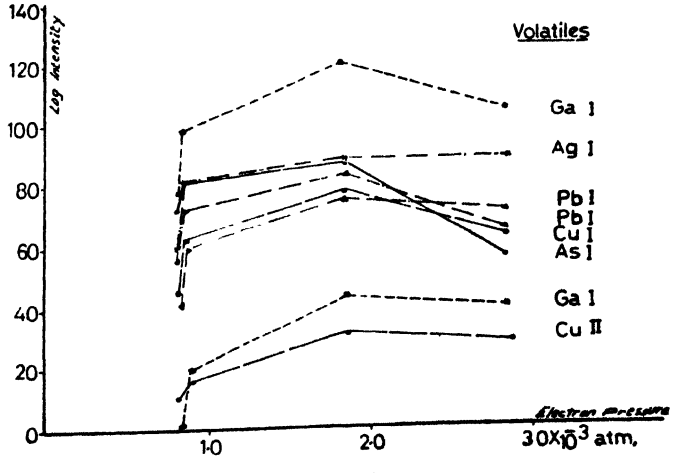


Fig. 14(a)

Calcium carbonate Figure 14 : Calcium carbonate matrix affords a reasonable range of electron pressure. Within this range, the intensity of either volatile or involatile elements exhibits maxiumum intensity.

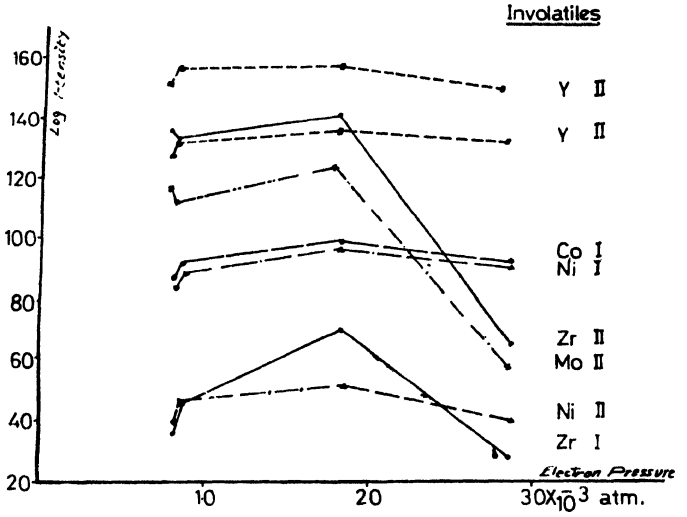


Fig. 14. Line intensity and electron pressure in case of $CaCO_3$ matrix.

Silicon dioxide Figure 15 : For volatile elements : the increase of electron pressure is accompanied with an increase in the line intensity for copper, gallium, lead and silver. Arsenic exhibits no variation with the increase of the electron

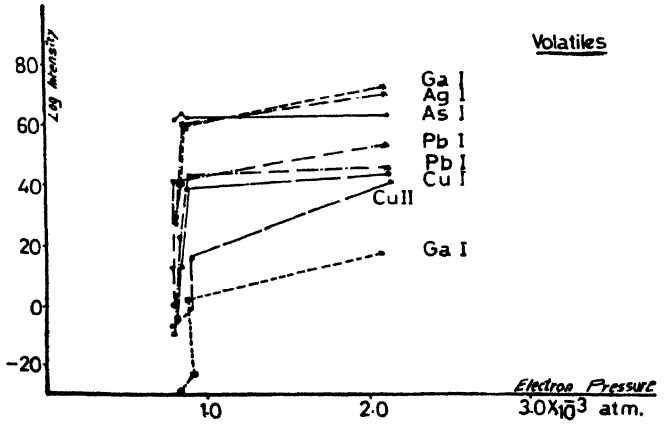


Fig. 15(a)

pressure. For involatile elements : cobalt, nickel and yttrium show no variation with increasing the electron pressure. The intensities of molybdenum and zirconium decrease with increasing electron pressure.

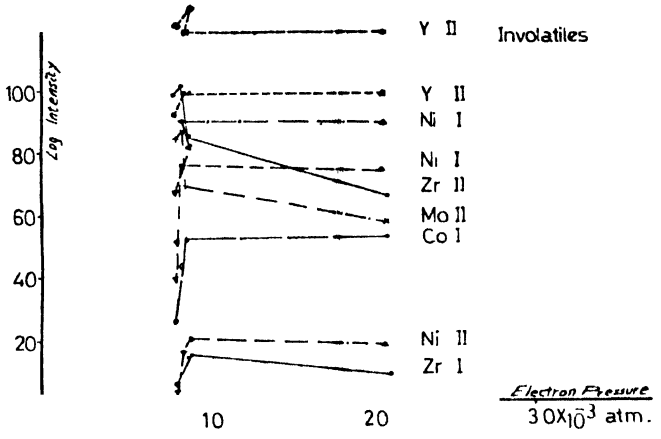
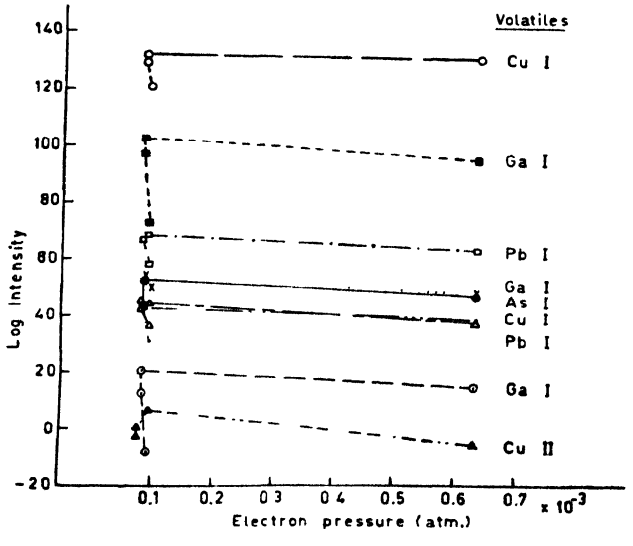


Fig. 15. Line intensity and electron pressure in case of SiO_2 matrix.

Sodium carbonate Figure 16 : This matrix affords the lowest values of electron pressure. Its values extend between $0.08-0.7\times10^{-3}$ atm. The reason could be because of the lower ionization potential of sodium (5.14 eV).



Fig, 16(a)

Generally for volatiles, the intensity shows minimum value at the beginning of the curve. On the contrary for involatiles, the intensity shows maximum value also at the first part of the curve.

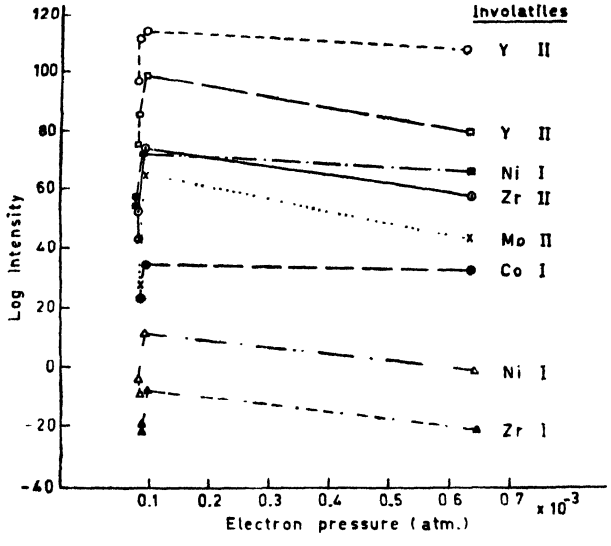


Fig. 16. Line intensity and electron pressure in case of Na_2CO_3 matrix.

General Discussion

From the above discussion, the main results achieved in this work could be summarized as follows :

(1) Noticeable variation in line intensity corresponding to trace elements with different matrices has been observed, e.g. the intensity of copper line varied from 38 in sodium carbonate matrix to 79 in aluminium oxide matrix, i.e. more than two fold variation. For the involatile element cobalt, the variation is more than three times in the same matrices. The line intensity of cobalt changes from 35 to 108 as in Figure (7 & 8). Consequently, the presence of an extraneous element in an unknown sample and not found in standards led resultant intensity provide false concentrations. This results confirms the well-known fact that samples and prepared standards should be similar in both physical and chemical characteristics.

(2) The variation of line intensity for every trace has even occured with different dilutions of each matrix, e.g. in silicon dioxide matrix, the intensity of gallium line varies from 28 to 71 while for zirconium it varies from 100 to 67.

Again this result ensures the known phenomena that for samples with diverse concentrations of the major constituents the working curves should include a study of the affect of the variation of each member on all the other constituents line intensity.

(3) In comparison with the four studied matrices, both aluminium oxide and calcium carbonate matrices, afford higher intensities for both volatile and involatile elements. Such behaviour could be useful. The detection limit of some elements having low sensitivity could be raised, only use the matrix that affords enhancement of their line intensity.

(4) On the contrary, the matrices, sodium carbonate and graphite exhibit lower intensities for all the studied elements. Again, line intensity of major constituents are always liable to self-absorption. Hence, one can employ the suitable matrix which causes suppression to line intensity of that element.

(5) The greatest arc temperature has been obtained with graphite matrix. Temperature measurement ascertained by previous publications. Somenova O.P. (1946) and Addink, N.W.H. (1957) proved that arcing different matrices, the arc temperature increases regularly with the increase of the ionization potential of the constituent gas of the arc column.

(6) Aluminium oxide and calcium carbonate matrices, relatively yield intermediate values of arc temperature. In the mean time, both these two matrices exhibit maximum line intensity for both volatile and involatile elements. Experimental results verified by theoretical proof reveal that for a given matrix the intensity of any spectral line varies with temperature according to a function with maximum.

(7) With different dilutions of sodium carbonate matrix between 12.5—75%, the resulting arc temperature varied between 5300—5620 °K. This variation relative to other matrices is high. Yet the variation in line intensity of both volatile and involatile elements relatively small. This variation for silver is between 48 & 54 and for yttrium is between 74 & 98. Smooth burning due to the presence of alkalie could be the cause of the resulting small variation in line intensity. Hence, sodium carbonate could be used as a buffer, specially for specimens like ores, which naturally have diverse concentrations of the major constituents.

Regarding the relation between electron pressure and line intensity due to matrix effect the discussion is still carried on. Yet experimental measurements reached at in this paper would lighten up the behaviour of this property with different matrices.

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